

04 MAY 2001

FORM PTD-1390 (Modified)  
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

205888US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/807996

INTERNATIONAL APPLICATION NO.  
PCT/EP99/08265

INTERNATIONAL FILING DATE  
29 October 1999

PRIORITY DATE CLAIMED  
04 November 1998

TITLE OF INVENTION

MODIFIED CATIONIC POLYMERS, THEIR PREPARATION AND THEIR USE IN PAPERMAKING

APPLICANT(S) FOR DO/EO/US

Juergen DECKER, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☒ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report

Notice of Priority

PCT/IB/304

PCT/IB/308

Letter Regarding Translation of Annexes

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/807996

INTERNATIONAL APPLICATION NO.

PCT/EP99/08265

ATTORNEY'S DOCKET NUMBER

205888US0PCT

21. The following fees are submitted..

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1,000.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

☐ 20 ☐ 30

\$0.00

CLAIMS

NUMBER FILED

NUMBER EXTRA

RATE

Total claims

6 - 20 =

0

x \$18.00

\$0.00

Independent claims

1 - 3 =

0

x \$80.00

\$0.00

Multiple Dependent Claims (check if applicable).

☐

\$0.00

TOTAL OF ABOVE CALCULATIONS =

\$860.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

☐

\$0.00

SUBTOTAL =

\$860.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).

☐ 20 ☐ 30

+

\$0.00

TOTAL NATIONAL FEE =

\$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐

\$0.00

TOTAL FEES ENCLOSED =

\$860.00

Amount to be:  
refunded  
charged

\$

\$

☒ A check in the amount of \$860.00

to cover the above fees is enclosed

☐ Please charge my Deposit Account No.

in the amount of

to cover the above fees

A duplicate copy of this sheet is enclosed

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



22850

Surinder Sachar  
Registration No. 34,423

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

May 4 2001

205888US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :  
JUERGEN DECKER ET AL : ATTN: APPLICATION DIVISION  
SERIAL NO: NEW US PCT APPLN :  
(Based on PCT NO:EP99/08265)  
FILED: HEREWITH : EXAMINER:  
FOR: MODIFIED CATIONIC POLYMERS,  
THEIR PREPARATION AND THEIR  
USE IN PAPERMAKING

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

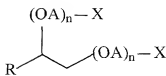
Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy to read as follows:

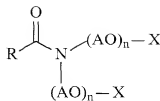
--3. (Amended) A modified cationic polymer as claimed in Claim 1, wherein

- (a) polyethyleneimines, polyamidoamines, polyamidoamines grafted with ethyleneimine, polymers containing vinylamine units or mixtures thereof are reacted with
- (b) at least one compound of the formula



(IV)

or



(V)

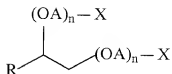
where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

4. (Amended) A process for the preparation of a modified cationic polymer as claimed in claim 1, wherein

- (a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with
- (b) compounds which are at least bifunctional with respect to NH groups and have at least one alkyl or alkenyl radical of at least 8 carbon atoms and, as a functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

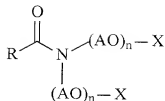
6. (Amended) A process as claimed in claim 4, wherein

- (a) compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with
- (b) at least one compound of the formula



(IV)

or



(V)

where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub> to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.--

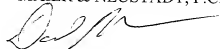
Please cancel Claim 7.

#### REMARKS

Claims 1-6 are active in the present application. The claims are amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
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**22850**

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**Marked-Up Copy**

Serial No: \_\_\_\_\_

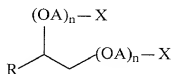
Amendment Filed on: \_\_\_\_\_

**IN THE CLAIMS**

3. (Amended) A modified cationic polymer as claimed in [either of claims 1 and 2]

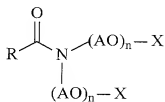
Claim 1, wherein

- (a) polyethyleneimines, polyamidoamines, polyamidoamines grafted with ethyleneimine, polymers containing vinylamine units or mixtures thereof are reacted with
- (b) at least one compound of the formula



(IV)

or



(V)

where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

4. (Amended) A process for the preparation of a modified cationic polymer as claimed in [any of claims 1 to 3] claim 1, wherein

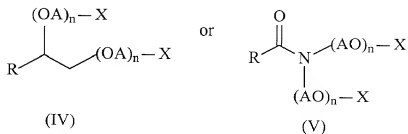
- (a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines,

polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with

- (b) compounds which are at least bifunctional with respect to NH groups and have at least one alkyl or alkenyl radical of at least 8 carbon atoms and, as a functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

6. (Amended) A process as claimed in claim 4 [or 5], wherein

- (a) compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with
- (b) at least one compound of the formula



where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub> to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.--

Cancel Claim 7.

Modified cationic polymers, their preparation and their use in papermaking

- 5 The present invention relates to modified cationic polymers which are obtainable by reacting water-soluble polymeric compounds containing NH groups with crosslinking agents, processes for their preparation and their use in papermaking.
- 10 EP-A-0438707 discloses a process for the production of paper, board and cardboard by draining paper stock containing interfering substances in the presence of hydrolyzed homo- and/or copolymers of N-vinylformamide having a degree of hydrolysis of at least 60% and cationic retention aids.
- 15 To inhibit the deposition of pitch in papermaking, according to the process of EP-A-0649941 a water-soluble polymer which contains at least 5 mol% of an N-alkyl-N-vinylcarboxamide, N-vinylformamide, N-vinylacetamide or partially hydrolyzed
- 20 N-alkyl-N-vinylcarboxamides is added to the paper stock.
- US-A-5536370 discloses condensates of polyalkylenepolyamines which are converted into crosslinked polyalkylenepolyamines by partial amidation of polyalkylenepolyamines and subsequent
- 25 condensation of the partially amidated polyalkylenepolyamines with at least bifunctional crosslinking agents. These products are used in papermaking as fixing agents for soluble interfering substances.
- 30 The non-prior-published DE-A-19719059.6 discloses reaction products of amino-containing polymers with reactive sizes, in particular alkyldiketenes. The reaction products are used as fixing agents for water-soluble and for water-insoluble interfering substances in the production of paper, board and
- 35 cardboard from paper stocks containing interfering substances.

US-A-5324787 discloses modified polymers which contain vinylamine units and are obtainable by reacting polymers containing vinylamine units with saturated aliphatic or aromatic glycidyl

40 ethers. The reaction products are used as flocculants and for increasing the retention of crills in papermaking. The aliphatic glycidyl ethers used for the modification contain from 1 to 18, particularly 4 to 12, carbon atoms in the alkyl group. The use of butyl glycidyl ether as a modifier is preferred.



JP-A-10-035090 discloses polymers which are obtainable by reacting water-soluble polymeric compounds which contain NH groups and which contain, as polymerized units, monomers 5 containing carboxyl groups and/or anhydride groups or amino groups and/or monomers containing quaternary ammonium salt groups with crosslinking agent which contain two or more oxazolinyl and/or oxazolidinyl groups. The reaction products are used for the waterproofing of inkjet papers.

10

It is an object of the present invention to provide novel polymers which are effective as fixing agents in papermaking.

We have found that this object is achieved, according to the 15 invention, by modified cationic polymers which are obtainable by reacting

(a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the 20 polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units with

(b) compounds which are at least bifunctional with respect to NH 25 groups and contain at least one alkyl or alkylene radical of at least 8 carbon atoms and, as functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

30 The present invention furthermore relates to a process for the preparation of modified cationic polymers by reacting

(a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the 35 polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units with

(b) compounds which are at least bifunctional with respect to NH 40 groups and have at least one alkyl or alkylene radical of at least 8 carbon atoms and, as functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

45 Compounds of group (a) are essentially water-soluble polymers containing amino and/or ammonium groups. Examples of such polymers are polyalkylenepolyamines, such as diethylenetriamine,

- triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, 3-(2-aminoethyl)aminopropylamine, 2-(diethylamino)ethylamine, 3-(dimethylamino)propylamine, dimethyldipropylentriamine, 4-aminoethyloctane-1,8-diamine,
- 5 3-(diethylamino)propylamine, N,N-diethyl-1,4-pentanediamine, dipropylenetriamine, bis(hexamethylene)triamine, N,N-bis(aminopropyl)methylamine, N,N-bis(aminopropyl)ethylamine, N,N-bis(aminopropyl)hexylamine, N,N-bis(aminopropyl)octylamine, N,N-dimethyldipropylenetriamine,
- 10 N,N-bis(3-dimethylaminopropyl)amine, N-(aminoethyl)butylenediamine, N-(aminopropyl)butylenediamine, bis(aminopropyl)butylenediamine and polyethyleneimines. Preferably used polyalkylenepolyamines are polyethyleneimines which are prepared, for example, by polymerizing ethyleneimine in
- 15 aqueous solution in the presence of acid-eliminating compounds, acids or Lewis acids. The polyethyleneimines have, for example, molar masses of from 1,000 to 5,000,000 g/mol. Polyethyleneimines having average molar masses of from 5,000 to 800,000 g/mol are particularly preferred.
- 20 Further suitable water-soluble, polymeric compounds containing NH groups are polyamidoamines which are obtainable, for example, by condensing dicarboxylic acids with polyamines. Suitable polyamidoamines are obtained, for example, by reacting
- 25 dicarboxylic acids of 4 to 10 carbon atoms with polyethyleneimines (average molar masses of from 300 to 1,000 g/mol) or with polyalkylenepolyamines which contain from 3 to 10 basic nitrogen atoms in the molecule. Suitable dicarboxylic acids are, for example, succinic acid, maleic acid, adipic acid,
- 30 glutaric acid, suberic acid, sebacic acid or terephthalic acid. In the preparation of the polyamidoamines, it is also possible to use mixtures of dicarboxylic acids as well as mixtures of a plurality of polyalkylenepolyamines. Suitable polyalkylenepolyamines are, for example, diethylenetriamine,
- 35 triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, tripropylenetetramine, dihexamethylenetriamine, aminopropylethylenediamine and bisaminopropylethylenediamine. For the preparation of the polyamidoamines, the dicarboxylic acids and
- 40 polyalkylenepolyamines are heated to relatively high temperatures, for example to temperatures of from 120 to 220°C, preferably from 130 to 180°C. The water formed in the condensation is removed from the system. In the condensation, lactones or lactams of carboxylic acids of 4 to 8 carbon atoms may, if
- 45 required, additionally be used. For example, from 0.8 to 1.4 mol of a polyalkylenepolyamine are used per mole of dicarboxylic

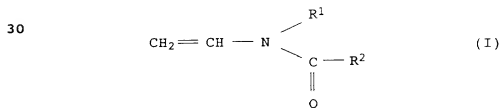
acid. The weight average molecular weights of the polyamidoamines are preferably at least 1,000 g/mol.

- 5 Further amino-containing polymers are polyamidoamines grafted with ethyleneimine. They are obtainable from the polyamidoamines described above by reaction with ethyleneimine in the presence of acids, such as sulfuric acid, or Lewis acids, e.g. boron trifluoride etherates, at, for example, from 80 to 100°C. For
- 10 example, from 1 to 100 parts by weight of ethyleneimine are grafted per 100 parts by weight of a polyamidoamine. Uncrosslinked polyamidoamines which may have been grafted with ethyleneimine are preferably used. Compounds of this type are described, for example, in DE-B-24 34 816.

- 15 Other suitable cationic polymers of group (a) are polyallylamines. Polymers of this type are obtained by homopolymerization of allylamine, preferably in a form neutralized with acids or in quaternized form, or by
- 20 copolymerization of allylamine with other monoethylenically unsaturated monomers, as described below as comonomers for N-vinylcarboxamides.

Further water-soluble, polymeric compounds of group (a) which

25 contain NH groups are polymers containing vinylamine units. They are prepared, for example, starting from open-chain N-vinylcarboxamides of the formula



- 35 where  $\text{R}^1$  and  $\text{R}^2$  may be identical or different and are each hydrogen or  $\text{C}_1$ - to  $\text{C}_6$ -alkyl. Suitable monomers are, for example, N-vinylformamide ( $\text{R}^1=\text{R}^2=\text{H}$  in formula I), N-vinyl-N-methylformamide, N-vinylacetamide,
- 40 N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methylpropionamide and N-vinylpropionamide. For the preparation of the polymers, said monomers can be polymerized either alone, as a mixture with one another or together with other monoethylenically unsaturated monomers. Preferably, homo-
- 45 or copolymers of N-vinylformamide are used as starting materials. Polymers containing vinylamine units are disclosed, for example, in US-A-4 421 602, EP-A-0 216 387 and EP-A-0 251 182. They are

obtained if polymers which contain the monomers of the formula I as polymerized units are hydrolyzed with acids, bases or enzymes.

- Examples of monoethylenically unsaturated monomers which are
- 5 copolymerized with the N-vinylcarboxamides are vinyl esters of saturated carboxylic acids of 1 to 6 carbon atoms, such as vinyl formate, vinyl acetate, vinyl propionate and vinyl butyrate, and vinyl ethers, such as C<sub>1</sub>- to C<sub>6</sub>-alkyl vinyl ethers, e.g. methyl or ethyl vinyl ether. Further suitable comonomers are ethylenically
  - 10 unsaturated C<sub>3</sub>- to C<sub>6</sub>-carboxylic acids, for example acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid and vinylacetic acid, and their alkali metal and alkaline earth metal salts, esters, amides and nitriles of said carboxylic acids, for example methyl acrylate, methyl methacrylate, ethyl acrylate and
  - 15 ethyl acrylate. Further suitable carboxylic esters are derived from glycols or polyalkylene glycols, in each case only one OH group being esterified, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, and hydroxybutyl methacrylate, and
  - 20 acrylic acid monoesters of polyalkylene glycols having a molar mass of from 500 to 10,000. Further suitable comonomers are esters of ethylenically unsaturated carboxylic acids with amino alcohols, for example dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate,
  - 25 diethylaminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate. The basic acrylates can be used in the form of the free bases, of the salts of mineral acids, such as hydrochloric acid, sulfuric acid
  - 30 or nitric acid, or of the salts with organic acids, such as formic acid, acetic acid, propionic acid or the sulfonic acids, or in quaternized form. Suitable quaternizing agents are, for example, dimethyl sulfate, diethyl sulfate, methyl chloride, ethyl chloride and benzyl chloride.
  - 35
- Further suitable comonomers are amides of ethylenically unsaturated carboxylic acids, such as acrylamide, methacrylamide and N-alkyl mono- and diamides of monoethylenically unsaturated carboxylic acids having alkyl radicals of 1 to 6 carbon atoms,
- 40 e.g. N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-propylacrylamide and tert-butylacrylamide, and basic (meth)acrylamides, such as dimethylaminoethylacrylamide, dimethylaminoethylmethacrylamide, diethylaminoethylacrylamide, diethylaminoethylmethacrylamide,
  - 45 dimethylaminopropylacrylamide, diethylaminopropylacrylamide,

dimethylaminopropylmethacrylamide and diethylaminopropylmethacrylamide.

- Furthermore, suitable comonomers are N-vinylpyrrolidone,
- 5 N-vinylcaprolactam, acrylonitrile, methacrylonitrile, N-vinylimidazole and substituted N-vinylimidazoles, e.g. N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole, N-vinyl-5-methylimidazole and N-vinyl-2-ethylimidazole, and N-vinylimidazolines, such as N-vinylimidazoline,
  - 10 N-vinyl-2-methylimidazoline and N-vinyl-2-ethylimidazoline. N-Vinylimidazoles and N-vinylimidazolines are used not only in the form of the free bases but also in a form neutralized with mineral acids or organic acids or in quaternized form, the quaternization preferably being effected with dimethyl sulfate,
  - 15 diethyl sulfate, methyl chloride or benzyl chloride. Dialkylammonium halides, e.g. dialkylammonium chlorides, are also suitable.

- Sulfo-containing monomers, for example vinylsulfonic acid,
- 20 allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, the alkali metal or ammonium salts of these acids or 3-sulfopropyl acrylate, are also suitable as comonomers for the compounds of the formula I. A further modification of the polymers containing vinylamine units can be achieved by
  - 25 copolymerizing up to 5 mol% of units of monomers having at least two ethylenically unsaturated double bonds. Such comonomers are usually used as crosslinking agents in copolymerizations. The presence of these comonomers during the copolymerization results in an increase in the molar masses of the copolymers. Suitable
  - 30 compounds of this type are, for example, methylenebisacrylamide, esters of acrylic acid and methacrylic acid with polyhydric alcohols, e.g. glycol diacrylate, glyceryl triacrylate, glycol dimethacrylate, glyceryl trimethacrylate and other polyols at least diesterified with acrylic acid or methacrylic acid, such as
  - 35 pentaerythritol and glucose. Other suitable crosslinking agents are divinylbenzene, divinylidioxane, pentaerythritol triallyl ether, pentaallylsucrose, divinylurea and divinylethyleneurea.

The copolymers contain, for example,

- 40 - from 99 to 1, preferably from 95 to 5, mol% of N-vinylcarboxamides of the formula I and
- from 1 to 99, preferably from 5 to 95, mol% of other monoethylenically unsaturated monomers copolymerizable
- 45 therewith

in polymerized form.

In order to prepare polymers containing vinylamine units, it is preferable to start from homopolymers of N-vinylformamide or from 5 copolymers which are preferably obtainable by copolymerizing

- N-vinylformamide with
- vinyl formate, vinyl acetate, vinyl propionate,
- 10 acrylonitrile, N-vinylcaprolactam, N-vinylurea, acrylic acid, N-vinylpyrrolidone or C<sub>1</sub>- to C<sub>6</sub>-alkyl vinyl ethers

and subsequently hydrolyzing the homopolymers or the copolymers with formation of vinylamine units from the polymerized

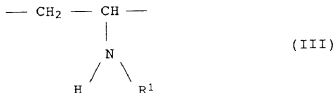
- 15 N-vinylformamide units, the degree of hydrolysis being, for example, from 0.1 to 100 mol%.

The hydrolysis of the polymers described above is carried out by the action of acids, bases or enzymes by known methods. The 20 polymerized monomers of the abovementioned formula I are converted by elimination of the group



25

where R<sup>2</sup> has the meanings stated in formula I, into polymers which contain vinylamine units of the formula



35

where R<sup>1</sup> has the meanings stated in formula I.

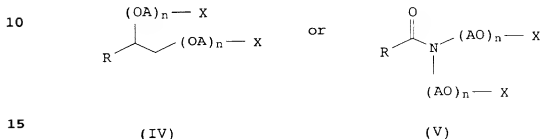
The homopolymers of the N-vinylcarboxamides of the formula I and 40 their copolymers may have a degree of hydrolysis of from 0.1 to 100, preferably from 1 to 99, mol%. In most cases, the degree of hydrolysis of the homo- and copolymers is from 5 to 95 mol%. The degree of hydrolysis of the homopolymers is equivalent to the content of vinylamine units in the polymers. In the case of 45 copolymers which contain vinyl esters as polymerized units, hydrolysis of the ester groups with formation of vinyl alcohol units may occur in addition to the hydrolysis of the

- N-vinylformamide units. This is the case in particular when the hydrolysis of the copolymers is carried out in the presence of sodium hydroxide solution. Copolymerized acrylonitrile is likewise chemically modified in the hydrolysis. Here, for example, amido or carboxyl groups form. The homo- and copolymers containing vinylamine units can, if required, contain up to 20 mol% of amidine units, which are formed, for example, by reaction of formic acid with two neighboring amino groups or by intramolecular reaction of an amino group with a neighboring amido group, for example of polymerized N-vinylformamide. The molar masses of the polymers containing vinylamine units are, for example, from 1,000 to 10 million, preferably from 10,000 to 5 million (determined by light scattering). This molar mass range corresponds, for example, to K values of from 5 to 300, preferably of from 10 to 250 (determined according to H. Fikentscher in 5% strength aqueous sodium chloride solution at 25°C and at a polymer concentration of 0.5% by weight).

- The polymers containing vinylamine units are preferably used in salt-free form. Salt-free aqueous solutions of polymers containing vinylamine units can be prepared, for example, from the salt-containing polymer solutions described above, with the aid of dialysis or ultrafiltration through suitable membranes with cut-offs of, for example, from 1,000 to 500,000, preferably from 10,000 to 300,000, Dalton. The aqueous solutions, described below, of other polymers containing amino and/or ammonium groups can also be obtained in salt-free form with the aid of dialysis or ultrafiltration. In the ultrafiltration through membranes having the abovementioned cut-offs, fractionation of the polymers resulting in polymers having a relatively narrow molar mass distribution  $M_w/M_n$  is achieved in addition to removal of salts which are formed, for example, in the hydrolysis of polymers containing N-vinylformamide units with acids or bases. The fractions of polymers having a narrow distribution which are obtained as retentate in the ultrafiltration give, on reaction with the compounds of group (b), reaction products which generally have higher activity than reaction products which are formed in the reaction of unfractionated polymers of the same composition with such compounds.

- The compounds (a) which contain NH groups and are preferably used for the preparation of the modified cationic polymers are polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units. The molar masses of the compounds (a) containing NH groups are preferably at least 1,000 g/mol.

The compounds of group (a) are reacted with compounds (b) which are at least bifunctional with respect to NH groups and contain at least one alkyl or alkenyl radical having at least 8 carbon atoms and, as a functional group, a halohydrin, epoxy, carboxyl, 5 chloroformate or isocyanate group or halogen atom. Preferred compounds of group (b) can be characterized, for example, with the aid of the following formulae:



where in each case R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, 20 chloroformate or isocyanate group or a halogen atom.

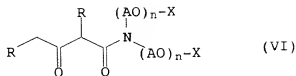
The compounds of the formula IV are obtainable starting from α-olefin-diols which may be alkoxyated and then provided with a functional group. Thus, for example, long-chain α-olefin-diols 25 are reacted with preferably from 5 to 20 mol of ethylene oxide, and a halohydrin group is introduced into the reaction product by reaction with epichlorohydrin. For example, from 0.5 to 2.5, preferably from 0.9 to 1.2, mol of epichlorohydrin are used per OH group. The halohydrin groups of the formula IV can be 30 converted into epoxy groups by treatment with, for example, aqueous bases.

The compounds of the formula V are obtained, for example, by reacting fatty acids having at least 8 carbon atoms in the 35 molecule with, for example, diethanolamine with amide formation and, if required, alkoxyating the resulting fatty acid amides then introducing a functional group. This can most simply be effected by reacting the fatty acid amide or the alkoxyated fatty acid amides with epichlorohydrin. This gives compounds of 40 the type of the formula V where X is a halohydrin group. By treatment with aqueous bases, epoxy groups are formed from the halohydrin groups.

Further compounds of group (b) can be characterized, for example, 45 with the aid of the formula



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where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is from 0 to 50 and X is a halohydrin, preferably chlorohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom, preferably a chlorine atom.

10

Compounds of the formula VI are obtained, for example, by reaction of diethanolamine with an alkylidiketene, such as stearyldiketene or oleyldiketene, alkoxylation, if required, with ethylene oxide, propylene oxide and/or butylene oxide, and

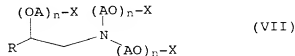
15 subsequent introduction of chlorohydrin groups by reaction with epichlorohydrin.

The corresponding epoxides can be prepared from the compounds of the formula VI by treatment with bases, if X is a halohydrin

20

group.  
Other suitable compounds of group (b) are compounds of the formula

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where

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R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl,

A is C<sub>2</sub>- to C<sub>4</sub>-alkylene,

n is 0-50 and

X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

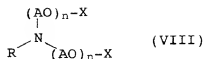
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Compounds of the formula VII are obtained, for example, from a long-chain α-olefin-epoxide (epoxide of 10 to 32 carbon atoms) by reaction with diethanolamine in a molar ratio of 1:3, alkoxylation, if required, with ethylene oxide, propylene oxide

40 and/or butylene oxide and reaction with epichlorohydrin.

Other compounds (b) can be prepared, for example, by alkoxyating C<sub>8</sub>- to C<sub>30</sub>-alkylamines and reacting the products thus obtainable with epichlorohydrin. Such compounds have the formula

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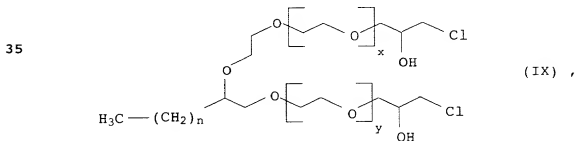
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where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl,  
 A is C<sub>2</sub>- to C<sub>4</sub>-alkylene,  
 n is 0-50 and  
 X is a halohydrin, epoxy, carboxyl, chloroformate or  
 10 isocyanate group or halogen atom.

The alkoxylation can be carried out with ethylene oxide, propylene oxide or butylene oxides. Ethylene oxide is preferably used. The ethoxylation of the long-chain (C<sub>10</sub> to C<sub>32</sub>)

- 15 α-olefin-diols, of the fatty amines or of the long-chain carboxamides is carried out in a manner known per se in the presence of the conventional catalysts, such as bases, e.g. alkali metal, alkaline earth metal or ammonium hydroxides, and of carbonates or alcoholates of alkali metals or alkaline earth  
 20 metals. The alkoxylation is effected, for example, in pressure-resistant autoclaves at from 60 to 230°C and, for example, from 1 to 10 bar. After the reaction, the reaction product is neutralized with acid and if necessary separated from the neutralized catalyst by filtration over a pressure filter, a  
 25 plate filter or a glass frit.

The addition of epichlorohydrin at the OH groups of the starting compounds is preferably effected in the presence of Lewis acids at from 50 to 150°C. Processes of this type are known, cf. DE-B  
 30 2434816. Particularly preferred compounds (b) are compounds of the formula



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where n is 5 - 27 and x and y are each 0 - 40, which are derived from α-olefin-diols.

- 45 The novel compounds are prepared by reacting at least one

(a) water-soluble polymeric compound containing NH groups with

(b) compounds which are at least bifunctional with respect to NH groups and have at least one alkyl or alkylene radical of at

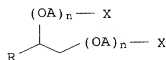
- 5 least 8 carbon atoms and, as a functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

The reaction of the compounds (a) and (b) is preferably carried  
10 out in aqueous solution at from 20 to 100°C with formation of aqueous solutions or dispersions. The weight ratio of the compounds (a) to the compounds (b) can be varied in a wide range and is, for example, from 15,000:1 to 1:1, preferably from 500:1 to 10:1. The ratios of the components (a) and (b) are chosen so  
15 that water-soluble or self-emulsifying polymers are formed. In a preferred embodiment of the novel process,

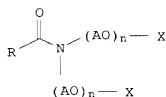
- a) compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines,  
20 polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with

(b) at least one compound of the formula

25



or



30

(IV)

(V)

where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n  
35 is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom. In the formulae IV and V, X is preferably an epichlorohydrin group or the epoxy group obtainable therefrom by treatment with bases.

- 40 The modified cationic polymers which are obtainable by reaction of the compounds of the groups (a) and (b) are used in papermaking as fixing agents for paper stocks containing interfering substances. The term papermaking includes the production of paper, board and cardboard by draining of paper  
45 stock. In papermaking, stickies are frequently the cause of production faults. Stickies are tacky impurities which enter the papermaking process together, for example, with the recycled

- fibers in the reprocessing of waste paper. Such impurities lead to deposits on wires, felts, rolls and other moving parts of the machines. Since the water circulations in the paper mills become increasingly concentrated, anionic impurities accumulate in the recycled water and greatly impair the efficiency of cationic polymeric process chemicals in the draining of paper stock and the retention of fillers and fibers. In practice, fixing agents are used for processing paper stocks containing such interfering substances. In the absence of fixing agents, for example, defects, generally in the form of thin parts or holes, form in the paper web, with the result that on the one hand the quality of the paper produced is adversely affected and on the other hand tears may be produced in the paper web in the paper machine.
- 15 The modified cationic polymers described above are effective fixing agents for interfering substances. The fixing agents can be used for processing all fiber qualities. Water is used in practice for the preparation of the paper stock that is at least partly or completely recycled from the paper machine. This is either clarified or unclarified white water or mixtures of such water qualities. As in the case of processed waste paper, the recycled water contains larger or smaller amounts of interfering substances. Possible sources of interfering substances and stickies, in addition to resins and lignin constituents which are formed as a result of cooking and mechanical processing of wood in fiber production, are mainly dispersions, natural colloidal systems, such as starch, caseins and dextrans, and hotmelt adhesives. These may be, for example, residual constituents of chemicals and printing inks from the de-inking process and binders from paper coating slips.

Specifically, they are resins, lignin residues, adhesives from spine gluing, from pressure-sensitive adhesive labels and from envelopes and binders from coating slips and printing inks. White pitch or sticky particles occur as particles of different size or in coarsely to finely dispersed form and in different amounts, depending on the recycled material introduced, and are often removed from the stock mixture only to an insufficient extent by flotation systems or mechanical stock processing and screening systems.

The content of such interfering substances in the paper stock can be characterized, for example, by the chemical oxygen demand (COD) a cumulative parameter. The COD values of such paper stocks are from 300 to 40,000, preferably from 1,000 to 30,000, mg of oxygen/kg of the aqueous phase of the paper stock. These amounts of interfering substances considerably impair the efficiency of

conventional cationic drainage and retention aids as long as they are used in papermaking in the absence of fixing agents.

- Suitable fibers for the preparation of the pulps are all
- 5 qualities conventionally used for this purpose, for example mechanical pulp, bleached and unbleached chemical pulp and paper stocks from all annual plants. Mechanical pulp includes, for example, groundwood pulp, thermomechanical pulp (TMP), chemothermomechanical pulp (CTMP), pressure groundwood,
  - 10 semi-chemical pulp, high-yield chemical pulp and refiner mechanical pulp (RMP). Suitable chemical pulps are, for example, sulfate, sulfite and soda pulps. The unbleached pulps, which are also referred to as unbleached kraft pulp, are preferably used. Suitable annual plants for the preparation of paper stocks are,
  - 15 for example, rice, wheat, sugar cane and kenaf. Pulps are also produced using waste paper and coated waste, which contains larger or smaller amounts of binder for coating slips and printing inks as well as starch, adhesives from pressure-sensitive adhesive labels and envelopes, dispersion
  - 20 residues from paper conversion and adhesives from spine gluing and hotmelts, either alone or as a mixture with other fibers. Pulps of the type described above contain larger or smaller amounts of interfering substances which, as explained above, can be characterized with the aid of the COD or with the aid of the
  - 25 cationic demand. The cationic demand is understood as meaning the amount of a cationic polymer which is required to bring a defined amount of the white water to the isoelectric point. Since the cationic demand is dependent to a very great extent on the composition of the cationic retention aid used in each case for
  - 30 the determination, a polyamidoamine which was obtained according to Example 3 of DE-C 2434816 from adipic acid and diethylenetriamine and was grafted with ethyleneimine and crosslinked with polyethylene glycol dichlorohydrin ether was used for standardization. The pulps containing interfering
  - 35 substances have COD values in the abovementioned range and have, for example, a cationic demand of more than 50 mg of polymer 1/l of white water.

- When paper stocks containing interfering substances are used, the
- 40 modified cationic polymers to be used according to the invention lead to a substantial reduction in the loads of interfering substances consisting of resins, stickies, white pitch and other anionic interfering substances, such as humic acids, wood extracts, lignin residues and ligninsulfate residues. Depending
  - 45 on the type of interfering substance, this manifests itself, for example, in lower turbidity of the filtrate water, reduced COD and fewer defects in the paper, a lower frequency of tearing of

the paper web, shorter downtimes and cleaning times and a lower level of deposition on moving machine parts. The fixing agents thus help to increase the productivity of paper and cardboard machines. In many cases, the modified cationic polymers to be used according to the invention additionally support the retention and drainage and thus significantly improve the runnability of the machines in the papermaking process. The modified cationic polymers are used in papermaking, for example, in amounts of from 0.01 to 2, preferably from 0.02 to 1.0, % by weight, based on dry paper stock.

The fixing agents to be used according to the invention can, if required, be used with further conventional process chemicals for papermaking. Such process chemicals are, for example, retention aids. These are, for example, polyethyleneimines, polyamines having molar masses of more than 50,000, polyamides which may be grafted with ethyleneimine, polyetheramines, polyvinylimidazoles, polyvinylpyrrolidines, polyvinylimidazoles, polydialkylldiaminoalkyl vinyl ethers, and polydialkylaminoalkyl (meth)acrylates in protonated or quaternized form. Further suitable retention aids are, for example, polydiallyldialkylammonium halides, in particular polydiallyldimethylammonium chloride. Particularly preferred retention aids are the crosslinked polyamidoamines which are described in DE-C-2434816 and are obtainable by condensation of dicarboxylic acids, such as adipic acid, with polyalkylenepolyamines, such as diethylenetriamine, grafting of the polyamidoamines with ethyleneimine and reaction of the ethyleneimine-grafted products with dichlorohydrin ethers of polyalkylene glycols. Other commercial retention aids are, for example, copolymers of acrylamide or methacrylamide and dialkylaminoalkyl acrylates or dialkylaminoalkyl methacrylates, for example copolymers of acrylamide and N,N-dimethylaminoethyl acrylate or copolymers of acrylamide and N,N-diethylaminoethyl acrylate. The basic acrylates are preferably used in a form neutralized with acid or in quaternized form. The quaternization can be effected, for example, with methyl chloride, dimethyl sulfate or benzyl chloride. The cationic retention aids have, for example, Fikentscher K values (determined in 5% strength aqueous sodium chloride solution at a polymer concentration of 0.5% by weight and a temperature of 25°C) of at least 140. The retention aids are usually used in papermaking in amounts of from 0.02 to 1.0% by weight, based on dry paper stock.

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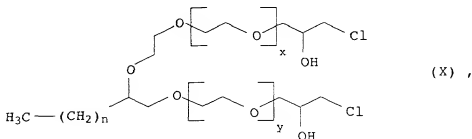
The K values were determined according to H. Fikentscher, Cellulose-Chemie, 13 (1932), 58 - 64 and 71 - 74, in 5% strength aqueous sodium chloride solution at a polymer concentration of 0.5% and a temperature of 25°C.

5

## Example 1

- 860 g of a 25% strength aqueous polyethyleneimine solution were initially taken in a 2 l four-necked flask which was equipped with a stirrer, a reflux condenser and an internal thermometer. The polyethyleneimine had an average molecular weight  $M_w$  of 750,000 g/mol. The aqueous polymer solution was heated to 60°C with vigorous stirring, and 7.03 g of the compound of the formula

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- where n was 17-21, x was 9 and y was 10, were added at this temperature. The reaction mixture was stirred for 2 hours at this temperature. A slightly yellow, turbid solution having a viscosity of 460 mPas (measured in a Brookfield viscometer, spindle 2, 23°C) was obtained.

## 30 Example 2

- 190 g of a 13.5% strength aqueous polyvinylformamide solution were initially taken in a 1 l four-necked flask which was equipped with a stirrer, a reflux condenser and a thermometer. The polyvinylformamide had a K value of 89 ( $M_w = 250,000$  g/mol). The polymer solution was stirred and was heated to 80°C. 10 g of a 50% strength aqueous sodium hydroxide solution (125 mmol) were added in the course of 10 minutes and the reaction mixture was then stirred for a further 2 hours at 80°C. 200 g of an aqueous polymer solution having a polymer content of 11.8% were obtained. The polymer contained 67 mol% of vinylformamide units and 33 mol% of vinylamine units. The polymer solution was cooled to 60°C, and 0.054 g of the compound of the formula X described in Example 1 was added at this temperature. The reaction mixture was stirred for 2 hours at 60°C and then cooled to room temperature. A slightly turbid solution was obtained.

## Example 3

- 500 g of a 9.6% strength aqueous solution of a modified polyethyleneimine which had been prepared according to Example 3 of DE-C-2434816 by grafting a polyamidoamine obtained from adipic acid and polyalkylenepolyamine with ethyleneimine and then crosslinking with polyethylene glycol dichlorohydrin ether and had been subjected to an ultrafiltration were initially taken in a 1 l four-necked flask which was equipped with a stirrer, a reflux condenser and an internal thermometer, the high molecular weight fraction (more than 500 kD) being isolated. The modified polyethyleneimine was heated to 60°C while stirring, and 0.530 g of the compound of the formula X described in Example 1 was added at this temperature. The reaction mixture was stirred for 2 hours at 60°C and then cooled to room temperature. A pale yellow, slightly turbid solution having a viscosity of 112 mPa.s (Brookfield viscometer, spindle number 1, 23°C) was obtained.

## Comparative Example 1 (Example 1 of US-A-5536370)

- 799 g of an anhydrous polyethyleneimine having an average molecular weight  $M_w$  of 25,000 g/mol were initially taken in a flask which was equipped with a stirrer, a thermometer and a means for working under nitrogen and were heated to 140°C in a stream of nitrogen, and 69 g of propionic acid were added in the course of 30 minutes. The temperature was then increased to 180°C and the water of reaction was distilled off continuously over a period of 5 hours. 200 g of the polymer thus obtained were then diluted with 700 ml of water and heated to 70°C. 36.5 ml of a 21% strength aqueous solution of an  $\alpha,\omega$ -bischlorohydrin of a polyethylene glycol having a molecular weight of 400 g/mol were added a little at a time in the course of 3 hours. The reaction mixture was then stirred for a further 1 hour at 70°C and then brought to pH 8 with 85 g of an 85% strength formic acid. 1018 g of a 20.7% strength polymer solution having a viscosity of 884 mPa.s (Brookfield viscometer, spindle number 2, 20°C) were obtained.

## Example 4

- 0.16 g/l of an aqueous dispersion of latex particles which had been converted into a film and beaten up again was added as a sticky to an aqueous fiber suspension of TMP (thermomechanical pulp) having a consistency of 0.8%. The latex was an acrylate copolymer dispersion. The same amount (0.05%, based on TMP) of the polymer stated in each case in Table 1 was added in each case to samples of this paper stock, and, after thorough mixing, paper



sheets were formed on a Rapid-Köthen sheet former. The filtrate was tested for the particle content with the aid of a laser-optical method, cf. Nordic Pulp & Paper Research Journal, No. 1, 1994, 9, pages 26 - 30 and 36). Of decisive importance for the efficiency of the fixing agent is the relative total volume of the unfixed stickies with an added amount of fixing agent of 0.05% of polymer, because this amount corresponds roughly to the amounts used in the paper production process. The lower this value, the more efficient is the fixing agent.

Table 1

Polymer sample according to	Unfixed sticky volume in the filtrate [%]
Example 1	12
Example 2	9
Example 3	29
Comparative Example 1	38

Example 5

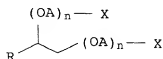
Example 4 was repeated, except that latex particles based on a styrene/butadiene copolymer were added in an amount of 0.16 g/l as interfering substance to TMP. The fixing agents used were the polymers stated in Table 2. After the addition of the polymers, the fiber was thoroughly mixed and drained on a Rapid-Köthen sheet former. The filtrate was then investigated for the content of sticky particles. Table 2 shows the relative volume of unfixed sticky particles.

Table 2

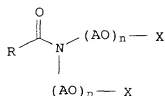
Polymer sample according to	Unfixed sticky volume in the filtrate [%]
Example 1	24
Example 2	16
Example 3	25
Comparative Example 1	44

We claim:-

1. A modified cationic polymer which is obtainable by reacting
  - (a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units with
    - (b) compounds which are at least bifunctional with respect to NH groups and contain at least one alkyl or alkylene radical of at least 8 carbon atoms and, as functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.
2. A modified cationic polymer as claimed in claim 1, wherein the compounds (a) containing NH groups have molar masses of at least 1,000 g/mol.
3. A modified cationic polymer as claimed in either of claims 1 and 2, wherein
  - (a) polyethyleneimines, polyamidoamines, polyamidoamines grafted with ethyleneimine, polymers containing vinylamine units or mixtures thereof are reacted with
    - (b) at least one compound of the formula



or



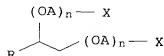
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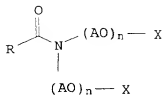
- where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.
4. A process for the preparation of a modified cationic polymer as claimed in any of claims 1 to 3, wherein

## 20

- (a) water-soluble, polymeric compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with
- (b) compounds which are at least bifunctional with respect to NH groups and have at least one alkyl or alkenyl radical of at least 8 carbon atoms and, as a functional group, a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.
5. A process as claimed in claim 4, wherein the reaction of the compounds (a) and (b) is carried out in aqueous solution at from 20 to 100°C with the formation of aqueous solutions or dispersions.
6. A process as claimed in claim 4 or 5, wherein
- (a) compounds containing NH groups and selected from the group consisting of the polyalkylenepolyamines, polyamidoamines, polyamidoamines grafted with ethyleneimine and polymers containing vinylamine units are reacted with
- (b) at least one compound of the formula



or



(IV)

(V)

where R is C<sub>8</sub>- to C<sub>30</sub>-alkyl or alkenyl, A is C<sub>2</sub>- to C<sub>4</sub>-alkylene, n is 0 - 50 and X is a halohydrin, epoxy, carboxyl, chloroformate or isocyanate group or a halogen atom.

7. The use of a cationically modified polymer as claimed in any of claims 1 to 3 in papermaking as a fixing agent for paper stocks containing interfering substances.

# Declaration, Power of Attorney

Page 1 of 4

0050/049509

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Modified cationic polymers, their preparation and their use in papermaking

the specification of which

☐ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP99/08265

on October 29, 1999

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.

Country

Day/Month/Year

Priority  
Claimed

19850817.4

Germany

04 November 1998

☒ Yes ☐ No

0050/049509

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,  
abandoned)

And we (I) hereby appoint:

Norman F. Oblon, Registration Number 24,618;  
 Marvin J. Spivak, Registration Number 24,913;  
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 William E. Beaumont, Registration Number 30,996;  
 Steven B. Kelber, Registration Number 30,073;  
 Jean-Paul Lavalleye, Registration Number 31,451;  
 Timothy R. Schwartz, Registration Number 32,171;  
 Stephen G. Baxter, Registration Number 32,884;  
 Richard L. Treanor, Registration Number 36,379;  
 Robert W. Hahl, Registration Number 33,893, our (my) attorneys, with full

powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Application papers not suitable for publication

SN 09807996

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